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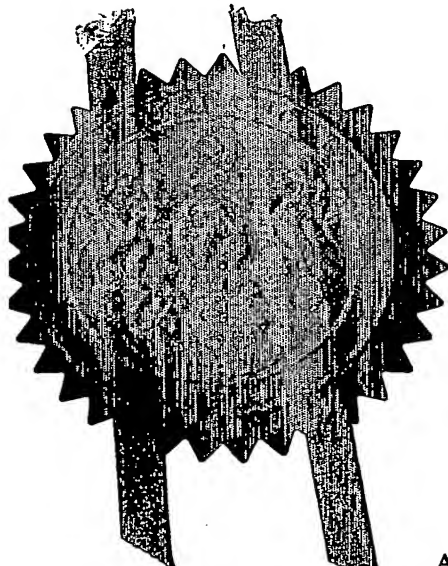
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Dated

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P01/7700 0.00-0213485.6

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9818

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0213485.6

12 JUN 2002

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4141891002

## 4. Title of the invention

PROCESS

## 5. Name of your agent (if you have one)

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BP INTERNATIONAL LIMITED  
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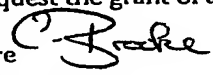
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### **PROCESS**

The present invention relates to a process for the production of acetic acid and in particular to a process for the production of acetic acid by carbonylation in the presence of an iridium catalyst, methyl iodide co-catalyst, and a promoter.

5        The production of acetic acid by the carbonylation of methanol in the presence of an iridium catalyst and a promoter such as ruthenium is described, for example, in EP-A-0752406, EP-A-0849248, EP-A-0849249, and EP-A-1002785.

10        WO-A-95/31426 discloses a process for the production of carboxylic acids or their esters having (n+1) carbon atoms by the liquid phase reaction of carbon monoxide with at least one alcohol having (n) carbon atoms in the presence of a catalytic system based on a compound of iridium and a halogen co-catalyst. The process is characterised by maintaining in the reaction medium water in a volume between greater  
15        than 0 and 10%, typically between 0.5 and 8%, preferably between 2 and 8%; the ester corresponding to the carboxylic acid and the alcohol in a volume varying between 2 and 40%; and iodides in soluble form of such a nature that the atomic ratio of the iodides to iridium is between greater  
20        than 0 and 10, typically between greater than 0 and 3, preferably between greater than 0 and 1.5. The volume of halogen co-catalyst in the reaction medium is between greater than 0 and 10%; typically between 0.5 and 8%, and preferably between 1 and 6%. Suitable iodides include alkaline

earth metal and alkali metal iodides, and specifically lithium iodide. The process of WO-A-95/31426 is otherwise unpromoted.

EP-A-0643034 describes a process for the carbonylation of methanol and/or a reactive derivative thereof in the presence of acetic acid, an iridium catalyst, methyl iodide, at least a finite concentration of water, methyl acetate and a promoter selected from ruthenium and osmium. In EP-A-0643034 it is said that ionic contaminants such as, for example, (a) corrosion metals, particularly nickel, iron and chromium and (b) phosphines or nitrogen-containing compounds or ligands which may quaternise in situ should be kept to a minimum in the liquid reaction composition as these will have an adverse effect on the reaction by generating I<sup>-</sup> in the liquid reaction composition which has an adverse effect on the reaction rate. Similarly, it is said, contaminants such as alkali metal iodides, for example lithium iodide, should be kept to a minimum.

In WO-A-96/237757 which is directed to the preparation of iridium carboxylates and their use in inter alia carbonylation reactions, the use of promoters not being mentioned, it is stated in contrast to WO-A-95/314326 that alkaline or alkaline earth ions are preferably eliminated, since their presence may have a harmful influence on the kinetics and selectivity of subsequent reactions in which the iridium carboxylate will be used as catalyst.

Under certain operating conditions, it has been observed that a catalyst system (iridium and ruthenium promoter) may precipitate. An effective method of ensuring that catalyst and promoter losses are reduced is to add a stabilising compound which prevents or at least mitigates precipitation of the catalyst system from the process streams. This is particularly important in the acetic acid product recovery streams since, at some point after reaction, the level of carbon monoxide pressure is reduced and hence the probability of some catalyst system precipitating from solution is increased.

Precipitation of the catalyst system has also been observed to occur when the process is operated using relatively high concentrations of promoter, such as a molar ratio of Ru to Ir of at least 2 :1. Similarly, precipitation may also be a problem for other promoter species such as those containing osmium or rhenium.

Thus, there remains a need for an improved iridium-catalysed promoted carbonylation process in which catalyst and promoter losses are prevented or retarded.

The present invention solves the technical problem defined above by using low concentrations of certain selected iodides. These iodides reduce the generation of insoluble or sparingly soluble catalyst system species such as ruthenium containing complexes. The use of low concentrations of the iodides selected also provide the additional advantage that catalyst system stability may be improved without incurring a significant decrease in the carbonylation rate. In addition, use of the stabilising compound allows the use of reduced levels of carbon monoxide, particularly in a second reaction zone and/or acetic acid product recovery section, and hence allows economic benefits to be achieved.

Advantageously, low concentrations of the selected iodides may be used to reduce the level of catalyst system precipitate after it has been formed.

Accordingly, the present invention provides for the use of a compound selected from the group consisting of alkali metal iodides, alkaline earth metal iodides, metal complexes capable of generating I<sup>-</sup>, salts capable of generating I<sup>-</sup>, and mixtures of two or more thereof to stabilise the catalyst and/or promoter under reduced levels of carbon monoxide in a process for the production of acetic acid by carbonylating methanol and/or a reactive derivative thereof with carbon monoxide in a carbonylation reaction zone containing a liquid reaction composition

comprising an iridium carbonylation catalyst, methyl iodide co-catalyst, a finite concentration of water, acetic acid, methyl acetate, at least one promoter selected from ruthenium, osmium and rhenium and wherein the molar ratio of said compound to iridium is in the range [greater than 0 to 5]

5 : 1.

The present invention also provides a process for the production of acetic acid by carbonylating methanol and/or a reactive derivative thereof with carbon monoxide in a carbonylation reaction zone containing a liquid reaction composition comprising an iridium carbonylation catalyst, methyl  
10 iodide co-catalyst, a finite concentration of water, acetic acid, methyl acetate, at least one promoter selected from ruthenium, osmium and rhenium and a stabilising compound selected from the group consisting of alkali metal iodides, alkaline earth metal iodides, metal complexes capable of generating I<sup>-</sup>, salts capable of generating I<sup>-</sup>, and mixtures of two or  
15 more thereof wherein where the molar ratio of promoter to iridium is greater than 2 : 1, the molar ratio of stabilising compound to iridium is in the range [greater than 0 to 5] : 1.

The present invention further provides a process for the production of acetic acid by carbonylating methanol and/or a reactive derivative  
20 thereof with carbon monoxide in a carbonylation reaction zone containing a liquid reaction composition comprising an iridium carbonylation catalyst, methyl iodide co-catalyst, a finite concentration of water, acetic acid, methyl acetate, at least one promoter selected from ruthenium, osmium and rhenium and a stabilising compound selected from the group  
25 consisting of alkali metal iodides, alkaline earth metal iodides, metal complexes capable of generating I<sup>-</sup>, salts capable of generating I<sup>-</sup>, and mixtures of two or more thereof wherein where the molar ratio of promoter to iridium is 2: 1 or less, the molar ratio of stabilising compound to iridium is in the range [greater than 0 to less than 0.1] : 1 or [greater  
30 than 0.1 to less than 0.5] : 1

The reaction zone may comprise a conventional liquid-phase carbonylation reaction zone. The pressure of the carbonylation reaction in the first reaction zone is suitably in the range 15 to 200 barg, preferably 15 to 100 barg, more preferably 15 to 50 barg and yet more preferably 18 to 35 barg. The temperature of the carbonylation reaction in the first reaction zone is suitably in the range 100 to 300 °C, preferably in the range 150 to 220 °C.

Preferably, two reaction zones are used, the first and second reaction zones being maintained in separate reaction vessels with means for withdrawing from the first reaction vessel and passing to the second reaction vessel liquid reaction composition from the first reaction vessel with dissolved and/or entrained carbon monoxide. Such a separate second reaction vessel may comprise a section of pipe between the first reaction vessel and a liquid reaction composition flashing valve. Preferably the pipe is liquid full. Typically the pipe's length to diameter ratio may be about 12:1, though length to diameter ratios both higher and lower than this may be employed.

Typically, at least a portion of the liquid reaction composition together with dissolved and/or entrained carbon monoxide is withdrawn from the first reaction zone and at least a portion of the withdrawn liquid and dissolved and/or entrained carbon monoxide passed to a second reaction zone. Preferably substantially all the liquid reaction composition together with dissolved and/or entrained carbon monoxide withdrawn from the first reaction zone is passed to the second reaction zone.

The second reaction zone may be operated at a reaction temperature in the range 100 to 300°C, preferably in the range 150 to 230°C. The second reaction zone may be operated at a temperature higher than the first reaction zone, typically up to 20°C higher. The second reaction zone may be operated at a reaction pressure in the range 10 to 200 barg, preferably in the range 15 to 100 barg. Preferably, the reaction



pressure in the second reaction zone is equal to or less than the reaction pressure in the first reaction zone. The residence time of liquid reaction composition in the second reaction zone is suitably in the range 5 to 300 seconds, preferably 10 to 100 seconds.

- 5           The carbon monoxide reactant for the carbonylation reactions may be essentially pure or may contain inert impurities such as carbon dioxide, methane, nitrogen, noble gases, water and C<sub>1</sub> to C<sub>4</sub> paraffinic hydrocarbons. The presence of hydrogen in the carbon monoxide and generated in situ by the water gas-shift reaction is preferably kept low, for example, less than 1 bar partial pressure, as its presence may result in the formation of hydrogenation products. The partial pressure of carbon monoxide in the first and second reaction zones is suitably independently in the range 1 to 70 bar, preferably 1 to 35 bar and more preferably 1 to 15 bar.
- 10           There may be introduced to the second reaction zone carbon monoxide in addition to that introduced to the second reaction zone as dissolved and/or entrained carbon monoxide. Such additional carbon monoxide may be co-joined with the first liquid reaction composition prior to introduction to the second reaction zone and/or may be fed separately to one or more locations within the second reaction zone. Such additional carbon monoxide may contain impurities, such as for example H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>. The additional carbon monoxide may be comprised of high pressure off-gas from the first reaction zone which could advantageously allow the first reaction zone to be operated at a higher CO pressure with the resulting higher flow of carbon monoxide being fed to the second reaction zone. Additionally it could eliminate the requirement for a high pressure off-gas treatment.
- 15           The additional carbon monoxide may also be comprised of another carbon monoxide-containing gas stream such as for example a carbon monoxide-rich stream from another plant.

Preferably greater than 10%, more preferably greater than 25%, even more preferably greater than 50%, for example at least 95%, of the dissolved and/or entrained carbon monoxide in the withdrawn reaction composition from the first reaction zone is consumed in the second  
5 reaction zone.

In the process of the present invention, suitable reactive derivatives of methanol include methyl acetate, dimethyl ether and methyl iodide. A mixture of methanol and reactive derivatives thereof may be used as  
10 reactants in the process of the present invention. Water is required as co-reactant for ether or ester reactants. Preferably, methanol and/or methyl acetate are used as reactants.

At least some of the methanol and/or reactive derivative thereof will be converted to, and hence present as, methyl acetate in the liquid reaction composition by reaction with the carboxylic acid product or  
15 solvent. Preferably, the concentrations of methyl acetate in the liquid reaction compositions in the first and second reaction zones are independently in the range 1 to 70% by weight, more preferably 2 to 50% by weight, most preferably 3 to 35% by weight

Water may be formed in situ in the liquid reaction compositions, for  
20 example, by the esterification reaction between methanol reactant and acetic acid product. Water may be introduced independently to the first and second carbonylation reaction zones together with or separately from other components of the liquid reaction compositions. Water may be separated from other components of reaction compositions withdrawn  
25 from the reaction zones and may be recycled in controlled amounts to maintain the required concentration of water in the liquid reaction compositions. Preferably, the concentrations of water in the liquid reaction compositions in the first and second reaction zones are independently in the range 0.1 to 20% by weight, more preferably 1 to  
30 15% by weight, yet more preferably 1 to 10% by weight.

To maximise catalyst system stability during the acetic acid product recovery, the concentration of water in process streams containing catalyst system for recycle to the carbonylation reaction zones is preferably maintained at a concentration of at least 0.5 % by weight.

- 5 Preferably, the concentration of methyl iodide co-catalyst in the liquid carbonylation reaction compositions in the first and second reaction zones is independently in the range 1 to 20% by weight, preferably 2 to 16% by weight.

- 10 The iridium catalyst in the liquid reaction compositions in the first and second reaction zones may comprise any iridium-containing compound which is soluble in the liquid reaction compositions. The iridium catalyst may be added to the liquid reaction compositions in any suitable form which dissolves in the liquid reaction compositions or is convertible to a soluble form. Preferably the iridium may be used as a
- 15 chloride free compound such as acetates which are soluble in one or more of the liquid reaction composition components, for example water and/or acetic acid and so may be added to the reaction as solutions therein. Examples of suitable iridium-containing compounds which may be added to the liquid reaction composition include  $\text{IrCl}_3$ ,  $\text{IrI}_3$ ,  $\text{IrBr}_3$ ,  $[\text{Ir}(\text{CO})_2\text{I}]_2$ ,
- 20  $[\text{Ir}(\text{CO})_2\text{Cl}]_2$ ,  $[\text{Ir}(\text{CO})_2\text{Br}]_2$ ,  $[\text{Ir}(\text{CO})_4\text{I}]^+\text{H}^+$ ,  $[\text{Ir}(\text{CO})_2\text{Br}_2]^+\text{H}^+$ ,  $[\text{Ir}(\text{CO})_2\text{I}_2]^+\text{H}^+$ ,  $[\text{Ir}(\text{CH}_3)_3(\text{CO})_2]^+\text{H}^+$ ,  $\text{Ir}_4(\text{CO})_{12}$ ,  $\text{IrCl}_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{IrBr}_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ir}_3(\text{CO})_{12}$ , iridium metal,  $\text{Ir}_2\text{O}_3$ ,  $\text{IrO}_2$ ,  $\text{Ir}(\text{acac})(\text{CO})_2$ ,  $\text{Ir}(\text{acac})_3$ , iridium acetate,  $[\text{Ir}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3][\text{OAc}]$ , and hexachloroiridic acid  $\text{H}_2[\text{IrCl}_6]$ , preferably, chloride-free complexes of iridium such as acetates, oxalates and
- 25 acetoacetates.

Preferably, the concentration of the iridium catalyst in the liquid reaction compositions of the first and second reaction zones is independently in the range 100 to 6000 ppm by weight of iridium.

The liquid reaction compositions in the first and second reaction zones additionally comprises one or more promoters. Suitable promoters are selected from ruthenium, osmium and rhenium, and are more preferably selected from ruthenium and osmium. Ruthenium is the most preferred promoter. The promoter may comprise any suitable promoter metal-containing compound which is soluble in the liquid reaction composition. The promoter may be added to the liquid reaction composition for the carbonylation reaction in any suitable form which dissolves in the liquid reaction composition or is convertible to soluble form.

Examples of suitable ruthenium-containing compounds which may be used as sources of promoter include ruthenium (III) chloride, ruthenium (III) chloride trihydrate, ruthenium (IV) chloride, ruthenium (III) bromide, ruthenium metal, ruthenium oxides, ruthenium (III) formate,  $[\text{Ru}(\text{CO})_3\text{I}_3]\text{-H}^+$ ,  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$ ,  $[\text{Ru}(\text{CO})_4\text{I}_2]$ ,  $[\text{Ru}(\text{CO})_3\text{I}_2]_2$ , tetra(aceto)chlororuthenium(II,III), ruthenium (III) acetate, ruthenium (III) propionate, ruthenium (III) butyrate, ruthenium pentacarbonyl, trirutheniumdodecacarbonyl and mixed ruthenium halocarbonyls such as dichlorotricarbonylruthenium (II) dimer, dibromotricarbonylruthenium (II) dimer, and other organoruthenium complexes such as tetrachlorobis(4-cymene)diruthenium(II), tetrachlorobis(benzene)diruthenium(II), dichloro(cycloocta-1,5diene) ruthenium (II) polymer and tris(acetylacetonate)ruthenium (III).

Examples of suitable osmium-containing compounds which may be used as sources of promoter include osmium (III) chloride hydrate and anhydrous, osmium metal, osmium tetraoxide, triosmiumdodecacarbonyl,  $[\text{Os}(\text{CO})_4\text{I}_2]$ ,  $[\text{Os}(\text{CO})_3\text{I}_2]_2$ ,  $[\text{Os}(\text{CO})_3\text{I}_3]\text{-H}^+$ , pentachloro- $\mu$ -nitrodiosmium and mixed osmium halocarbonyls such as tricarbonyldichloroosmium (II) dimer and other organoosmium complexes.

Examples of suitable rhenium-containing compounds which may be used as sources of promoter include  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Re}(\text{CO})_5\text{Cl}$ ,  $\text{Re}(\text{CO})_5\text{Br}$ ,  $\text{Re}(\text{CO})_5\text{I}$ ,  $\text{ReCl}_3 \cdot x\text{H}_2\text{O}$ ,  $[\text{Re}(\text{CO})_4\text{I}]_2$ ,  $\text{Re}(\text{CO})_4\text{I}^+\text{H}^-$  and  $\text{ReCl}_5 \cdot y\text{H}_2\text{O}$ .

Preferably, the promoter is present in an effective amount up to the limit of its solubility in the liquid reaction composition and/or any liquid process streams recycled to the carbonylation reactor from the acetic acid recovery stage. The promoter is suitably present in the liquid reaction composition at a molar ratio of promoter to iridium of [2.5 to 15]:1, preferably [2.5 to 10]:1, more preferably [4 to 10]:1. A suitable promoter concentration is less than 8000 ppm, such as 400 to 7000 ppm.

The liquid reaction compositions also comprise a stabilising compound selected from alkali metal iodides, alkaline earth metal iodides, metal complexes capable of generating I<sup>-</sup>, salts capable of generating I<sup>-</sup>, and mixtures of two or more thereof. Suitable alkali metal iodides include lithium iodide, sodium iodide and potassium iodide. Suitable alkaline earth metal iodides include calcium iodide. Suitable metal complexes capable of generating I<sup>-</sup> include complexes of the lanthanide metals, for example, samarium and gadolinium, cerium, and other metals such as molybdenum, nickel, iron, aluminium and chromium. Salts capable of generating I<sup>-</sup> include, for example, acetates which are capable of conversion in-situ to I<sup>-</sup> typically LiOAc and organic salts, such as quaternary ammonium iodides and phosphonium iodides, which may be added as such. A preferred stabilising compound is lithium iodide.

Suitably, the amount of stabilising compound used is such that it is effective in providing an increase in the solubility of the catalyst system and preferably, does not significantly decrease the carbonylation reaction rate.

The amount of stabilising compound introduced to the liquid reaction compositions should be selected to take account of the presence of I<sup>-</sup> from other sources because it is believed that an excessive amount

of I- in the liquid reaction compositions may be detrimental. The optimum ratio of the stabilising compound is selected depending on the nature of the chosen iodide compound, the counter ion, the degree of dissociation in the carbonylation medium and the molar ratio of promoter : iridium used.

It has been found that a molar ratio of stabilising compound : iridium in the range [greater than 0 to 5] : 1 is effective in providing increased stability of the catalyst system and, in particular, where the molar ratio of promoter to iridium is greater than 2 : 1, for example at least 3 : 1 such as in the range [4 to 12] : 1. Where the molar ratio of promoter : iridium is 2 : 1 or less than 2 : 1, the molar ratio of stabilising compound : iridium is suitably in the range [greater than 0 to less than 0.1] : 1 or [greater than 0.1 to less than 0.5] : 1.

Preferably, where the molar ratio of promoter to iridium is greater than 2 : 1, such as in the range [greater than 2 to 12] : 1, for example, in the range [greater than 2 to 5] : 1, the molar ratio of stabilising compound to iridium is in the range [0.05 to 2] : 1, such as [0.05 to 0.5] : 1. Suitably, where the molar ratio of promoter to iridium is 4 : 1 or greater, such as in the range [4 : 10] : 1, the molar ratio of stabilising compound : iridium is in the range [0.05 to 0.5] : 1, for example, [0.15 to 0.5] : 1. Suitably, for a molar ratio of promoter to iridium of at least 5 : 1, such as in the range [greater than 5 to 12] : 1, for example, [6 : 10] : 1, the molar ratio of stabilising compound to iridium is preferably in the range [0.05 to 2] : 1, for example [0.15 : 1.5] : 1.

Preferably, the promoter is ruthenium and the stabilising compound is selected from lithium iodide, sodium iodide, potassium iodide, and quaternary ammonium and phosphonium iodides, most preferably, lithium iodide. Where these stabilising compounds are used and the ruthenium : iridium molar ratio is in the range [2 to 5] : 1, the molar ratio of the stabilising compound to iridium is preferably [0.05 to 0.5] : 1. Where the

molar ratio of ruthenium : iridium is greater than 5 : 1, preferably, the molar ratio of stabilising compound to iridium is [0.05 to 1.5] : 1. Where the ruthenium to iridium molar ratio of is about 4:1 or greater the molar ratio of stabilising compound to iridium may suitably be in the range [0.05 to 0.5]: 1, preferably in the range [0.15 to 0.5]: 1.

The stabilising compound may be introduced into the reaction zone(s) at any stage during the carbonylation reaction. The stabilising compound may be introduced directly into a reaction zone, for example, via a reactant-feed-stream-or-it-may-be-introduced-indirectly into a reaction zone, for example via a recycle stream such as a catalyst recycle stream. Where, catalyst system precipitate has already formed, for example, in the second reaction zone and/or in the product recovery section, the precipitate may be dissolved back into solution by the direct and/or indirect addition of the stabilising compound to the reaction zone(s).  
 15 Optionally, heat, agitation and/or increased carbon monoxide partial pressure may be employed to aid further the re-dissolution of the precipitate.

Acetic acid product may be recovered from the second reaction zone and optionally together with or separately from the first reaction zone by flash separation. In flash separation liquid reaction composition is passed to a flashing zone via a flashing valve. The flash separation zone may be an adiabatic flash vessel or may have additional heating means. In the flash separation zone a liquid fraction comprising the majority of the iridium catalyst and the majority of the promoter is separated from a vapour fraction comprising acetic acid, carbonylatable reactant, water and methyl iodide carbonylation co-catalyst and non-condensable gases such as nitrogen, carbon monoxide, hydrogen and carbon dioxide; the liquid fraction being recycled to the first reaction zone and the vapour fraction being passed to one or more distillation zones. In a first distillation zone  
 25  
 30 acetic acid product is separated from the light components (methyl iodide

and methyl acetate). The light components are removed overhead, and recycled to the first and/or second reaction zones. Also removed overhead is a low pressure off-gas comprising the non-condensable gases such as nitrogen, carbon monoxide, hydrogen and carbon dioxide. Such a low-pressure off-gas stream may be passed through an off-gas treatment section to remove condensable materials such as methyl iodide, prior to being vented to atmosphere, for example, via a flare.

The acetic acid produced by the process according to the present invention may be further purified by conventional processes, for example further distillation to remove impurities such as water, unreacted carbonylation reactant and/or ester derivative thereof and higher-boiling by-products.

The process of the present invention may be performed as a batch or as a continuous process, preferably as a continuous process.

The present invention will now be illustrated by way of example only and with reference to the following Examples.

#### **General Reaction Method**

All experiments were performed in a 300cm<sup>3</sup> zirconium autoclave, equipped with a stirrer and a liquid injection facility. The autoclave was pressure tested to 4x10<sup>6</sup> N/m<sup>2</sup> with nitrogen, then flushed three times with carbon monoxide up to 1x10<sup>6</sup> N/m<sup>2</sup>. An initial charge consisting of methyl acetate (approx 48.0g) acetic acid (approx 38.0g), methyl iodide (approx 13.3g) and water (approx 12.5g) was placed into the autoclave, which was then repurged with carbon monoxide and vented slowly to prevent loss of volatiles.

Carbon monoxide (approx 6-7x10<sup>5</sup> N/m<sup>2</sup>) was fed into the autoclave which was then heated, with stirring (1500 rpm) to 190°C. The catalyst injection system was primed with approx 5.6g of iridium acetate solution (5.25% Ir w/w, in acetic acid : water, 4 : 1) and acetic acid (approx



8.7g) and injected with an overpressure of carbon monoxide to bring the autoclave pressure to  $2.8 \times 10^6 \text{ N/m}^2$

The reaction rate was monitored by drop in carbon monoxide pressure from a ballast vessel, typically pressured to  $7 \times 10^6 \text{ N/m}^2$ . The autoclave was maintained at a constant temperature of  $190^\circ\text{C}$  and pressure of  $2.8 \times 10^6 \text{ N/m}^2$  throughout the reaction. The reaction was terminated when the drop in ballast pressure became less than  $1 \times 10^4 \text{ N/m}^2$  per 5 minutes.

After cooling, a gas analysis sample was taken, and the autoclave vented. The liquid components were discharged, and analysed for liquid by-products by known established gas chromatography methods. Detected components are quantified by integration of the component peaks relative to an external standard and expressed as parts per million (ppm) by weight.

In the batch reactions, 'Total' propanoic acid was defined as the sum of propanoic acid and its precursors ((ethyl acetate and ethyl iodide) converted to ppm propanoic acid) detected in the quenched liquid products of the batch reaction expressed in ppm.

The rate of gas uptake at a certain point in a reaction run was used to calculate the carbonylation rate, as number of moles of reactant consumed per litre of cold degassed reactor composition per hour ( $\text{mol/l/h}$ ) at a particular reactor composition (total reactor composition based on a cold degassed volume)

The methyl acetate concentration was calculated during the course of the reaction from the starting composition, assuming that one mole of methyl acetate was consumed for every mole of carbon monoxide that was consumed. No allowance was made for organic components in the autoclave headspace.

## **Examples**

### **Experiment A**

- A baseline experiment was performed with the autoclave charged with methyl acetate (48.05g) acetic acid (48.42g) ruthenium acetate (12.28g) water (13.86g) methyl iodide (13.31g). The catalyst solution consisted of an iridium solution (5.25% Ir w/w) with acetic acid (8.71g). The approximate ratio of iridium to ruthenium was 1:4. The rate of reaction, ~~based on carbon monoxide uptake was measured to be 19.6 mol/l/h~~ at a calculated reaction composition of 11% methyl acetate and steadily declined until virtually all the methyl acetate was consumed. Conversion to acetic acid was 99.66% based on methyl acetate consumed. Analysis of propanoic acid precursors gave a total propanoic acid make of 467.8 ppm. Gaseous by-products in the cold-vented off-gas were H<sub>2</sub> 3.6mmol; CO<sub>2</sub> 8.0 mmol and CH<sub>4</sub> 12.6 mmol. The cooled reaction mixture showed a clearly observable amount of solid material. These results are shown in Table 1.

### **Example 1**

- Experiment A was repeated with the autoclave charged with methyl acetate (48.05g) acetic acid (57.2g) ruthenium acetate (12.2g) water (13.83g) methyl iodide (13.34g) and lithium iodide (0.11g). The catalyst solution consisted of an iridium solution (5.25% Ir w/w). Conversion to acetic acid was 98.58% based on methyl acetate consumed. No precipitate was observed in the cooled reaction mixture even after several days. The results are shown in Table 1.

### **Example 2**

- Experiment A was repeated with the autoclave charged with methyl acetate (48.05g) acetic acid (57.2g) ruthenium acetate (12.2g) water (13.83g) methyl iodide (13.34g) and lithium iodide (0.0561g). The catalyst

solution consisted of an iridium solution (5.25% Ir w/w). Conversion to acetic acid was 98.94% based on methyl acetate consumed. No precipitate was observed in the cooled reaction mixture even after several days. The results are shown in Table 1.

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**Table 1**

Experiment	Ru : Ir	Li : Ir	Rate mol/l/h	Precipitate formed	Propanoic acid /ppm	H <sub>2</sub> /mmol	CO <sub>2</sub> /mmol	CH <sub>4</sub> /mmol
Experiment A	4 : 1	-	19.6	Yes	467.8	3.6	8.0	12.6
Example 1	4 : 1	0.5 : 1	17.9	No	296.5	3.0	8.1	13.8
Example 2	4 : 1	0.25 : 1	17.0	No	369.0	1.7	5.5	8.5

From Table 1 it can be seen that the iodide compound has a significant solubilising effect on the catalyst system and without incurring a significant decrease in carbonylation rate.

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**Experiment B**

A baseline experiment was performed with the autoclave charged with methyl acetate (48.06g) acetic acid (58.03g) ruthenium acetate (24.35g) water (12.01g) methyl iodide (13.30g). The catalyst solution consisted of an iridium solution (5.25% Ir w/w). The rate of reaction, based on carbon monoxide uptake was measured to be 22.2 mol/l/h at a calculated reaction composition of 11% methyl acetate and steadily declined until virtually all the methyl acetate was consumed. Conversion to acetic acid was 98.80% based on methyl acetate consumed. Analysis of propionic acid precursors gave a total propanoic acid make of 399.7 ppm. Gaseous by-products in the cold-vented off-gas were H<sub>2</sub>, 0.1 mmol; CO<sub>2</sub>, 0.3 mmol; CH<sub>4</sub>, 0.4 mmol. The cooled reaction mixture showed a significant amount of clearly visible precipitate. These results are shown in Table 2.

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**Example 3**

- Experiment B was repeated with the autoclave charged with methyl acetate (48.14g) acetic acid (58.08g) ruthenium acetate (24.34g) water (12.00g) methyl iodide (13.33g) and lithium iodide (0.1076g). Conversion to acetic acid was 98.55% based on methyl acetate consumed. No precipitate was observed in the cooled reaction mixture even after several days. The results are shown in Table 2.

**Example 4**

- Experiment B was repeated with the autoclave charged with methyl acetate (48.13g) acetic acid (58.02g) ruthenium acetate (24.35g) water (12.02g) methyl iodide (13.30g) and lithium iodide (0.052g). The catalyst solution consisted of an iridium solution (5.25% Ir w/w). Conversion to acetic acid was 98.63% based on methyl acetate consumed. No precipitate was observable in the cooled reaction mixture even after several days. The results are given in Table 2.

**Example 5**

- Experiment B was repeated with the autoclave charged with methyl acetate (48.01g) acetic acid (58.03g) ruthenium acetate (24.34g) water (12.05g) methyl iodide (13.34g) and lithium iodide (0.0333g). The catalyst solution consisted of an iridium solution (5.25% Ir w/w). Conversion to acetic acid was 98.81% based on methyl acetate consumed. No precipitate was observable in the cooled reaction mixture even after several days. The results are shown in Table 2.

**Example 6**

- Experiment B was repeated with the autoclave charged with methyl acetate (48.04g) acetic acid (58.03g) ruthenium acetate (24.37g) water (12.45g) methyl iodide (13.34g) and lithium iodide (0.0115g). The catalyst

solution consisted of an iridium solution (5.25% Ir w/w). Conversion to acetic acid was 98.50% based on methyl acetate consumed. The cooled reaction mixture showed small traces of precipitates. The results are shown in Table 2.

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**Table 2**

Experiment	Ru : Ir	Li : Ir	Rate mol/l/h	Precipitate formed	Propanoic acid /ppm	H <sub>2</sub> /mmol	CO <sub>2</sub> /mmol	CH <sub>4</sub> /mmol
Experiment B	8 : 1	-	22.2	Yes	399.7	0.1	0.3	0.4
Example 3	8 : 1	0.5 : 1	21.0	No	365.5	2.5	10.8	21.2
Example 4	8 : 1	0.25 : 1	20.8	No	348.6	2.7	10.8	21.0
Example 5	8 : 1	0.15 : 1	21.8	No	354.4	2.9	10.0	19.8
Example 6	8 : 1	0.05 : 1	22.0	trace	320.9	3.2	10.0	15.7

From Table 2 it can be seen that in Examples 3 to 5 the addition of an iodide compound has a significant solubilising effect on the catalyst

10 system and without incurring a significant decrease in reaction rate.

Where the lithium iodide stabilising compound is used at a Li : Ir molar ratio of 0.05 : 1 (Example 6) a solubilising effect on the catalyst system is achieved but the effect is less marked than at higher Li : Ir ratios.

